

ARMY RESEARCH LABORATORY



Tunable Diode Laser Diagnostics for Combustion Species

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| We report here on work employing tunable diode laser absorption spectroscopy to characterize premixed, low-pressure flames inhibited with halons and halon alternative agents. This characterization is in the form of spatial temperature and species concentration profiles of the flames. We report here the observation of 11 combustion species, including short-lived intermediates CF ₂ O and CF ₃ radical. | | | |
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1. INTRODUCTION

The main chemical agents used in fire suppression systems in military vehicles are Halon 1301 and Halon 1211 (CF_2ClBr). In accordance with the Copenhagen amendments to the Montreal Protocol (Fourth Meeting of the Parties to the Montreal Protocol 1992), the production and sale of these compounds, chlorofluorocarbons, and bromochloroflourocarbons, have been banned because of their role in the catalytic destruction of stratospheric ozone. Furthermore, their usage may be phased out completely before the present stockpile is exhausted. The Army Research Laboratory (ARL) has been involved in a project designed to identify suitable replacement compounds for use in future fire suppression systems, and for inclusion in present fire suppression systems on board Army vehicles.

We have employed tunable diode laser absorption spectroscopy (TDLAS) to characterize low-pressure premixed methane/oxygen/argon flames inhibited with Halon 1301 (CF_3Br) and the Halon alternative compounds FE-13 (CF_3H) and HFC-125 (C_2F_5H). This work is part of a larger project designed to help identify replacement fire-suppression compounds for the presently used Halon 1301. The Army's fire suppression need in weapon systems and crew compartments is one of the most stringent. TDLAS has been shown to be a versatile and powerful diagnostic technique to study combustion processes, and is presently being applied to other combustion systems, specifically diffusion flames and nonthermal plasmas.

The aspect of this project reported here is the application of tunable diode lasers as a diagnostic tool to characterize combustion systems. We have studied inhibited low-pressure premixed flames, using the TDLAS technique to measure the flame species' concentration and temperature profiles to characterize the combustion chemistry. The flames are doped with up to 1.0% of a halogenated compound. The results of this study are being used to validate a chemical kinetic mechanism (Westmoreland et al. 1994), which attempts to computationally model the behavior of halogenated flames (Babushok and Tsang 1994).

Tunable diode lasers offer the ability to observe individual ro-vibrational transitions of many flame species in a nonintrusive manner, and thus no perturbation of the combustion system occurs. This ability allows for qualitative and/or quantitative measurement of the production or destruction of a compound as a function of position in the flame. By observing ro-vibrational transitions, a species' temperature and concentration can be extracted from the observed spectra. To date, 11 different flame species (Table 1) have been observed in our laboratory.

Table 1. List of Species Detected using TDLAS

| Species | Frequency (cm ⁻¹) | Transition |
|--------------------------------|----------------------------------|---|
| CO | 2,020–2,100 | |
| CO ₂ | 2,020–2,100 | v ₃ |
| CH ₄ | 1,240–1,280 | v ₂ and v ₄ dyad |
| H ₂ O | 1,260–1,275 | v ₂ |
| CF ₄ | 1,250–1,280 | v ₃ and 2v ₄ |
| CF ₃ H | 1,075–1,100 | v ₂ |
| CF ₂ H ₂ | 1,075–1,120 | v ₃ |
| CF ₃ Br | 1,075–1,120 | v ₁ and v ₂ +v ₃ |
| CF ₃ I | 1,075–1,100 | v ₁ |
| CF ₂ O | 1,250–1,275 1,910–1,970 | v ₄ v ₁ |
| NO | 1,910–1,950 | |

2. EXPERIMENTAL

The details of the experimental apparatus have been previously described in detail (McNesby, Daniel, and Mizolek 1995a) and so will only be briefly discussed here. Figure 1 shows a schematic representation of the three major components of the system: the diode laser as radiation source, the gas handling system, and the data acquisition equipment. Each component will be discussed in the subsequent paragraphs.

The diode laser system (Laser Photonics, Analytics Division, Inc.) consists of a cryogenically cooled laser source, a monochromator, and liquid nitrogen (LN₂) -cooled infrared (IR) detectors. Laser diodes, which are lead salt crystals, produce multimode, monochromatic radiation at cryogenic temperatures (10–100 K) upon application of a small current across the diode. The frequency of the emitted radiation is selected by adjusting the temperature of the applied current to the diode. The linewidth of the radiation is typically 0.0005 cm⁻¹, which allows the detection of individual ro-vibration transitions of the molecules being studied. The emitted radiation passes through the monochromator, selecting the individual mode and thus the frequency of the radiation of interest for the experiment. The IR beam passes through

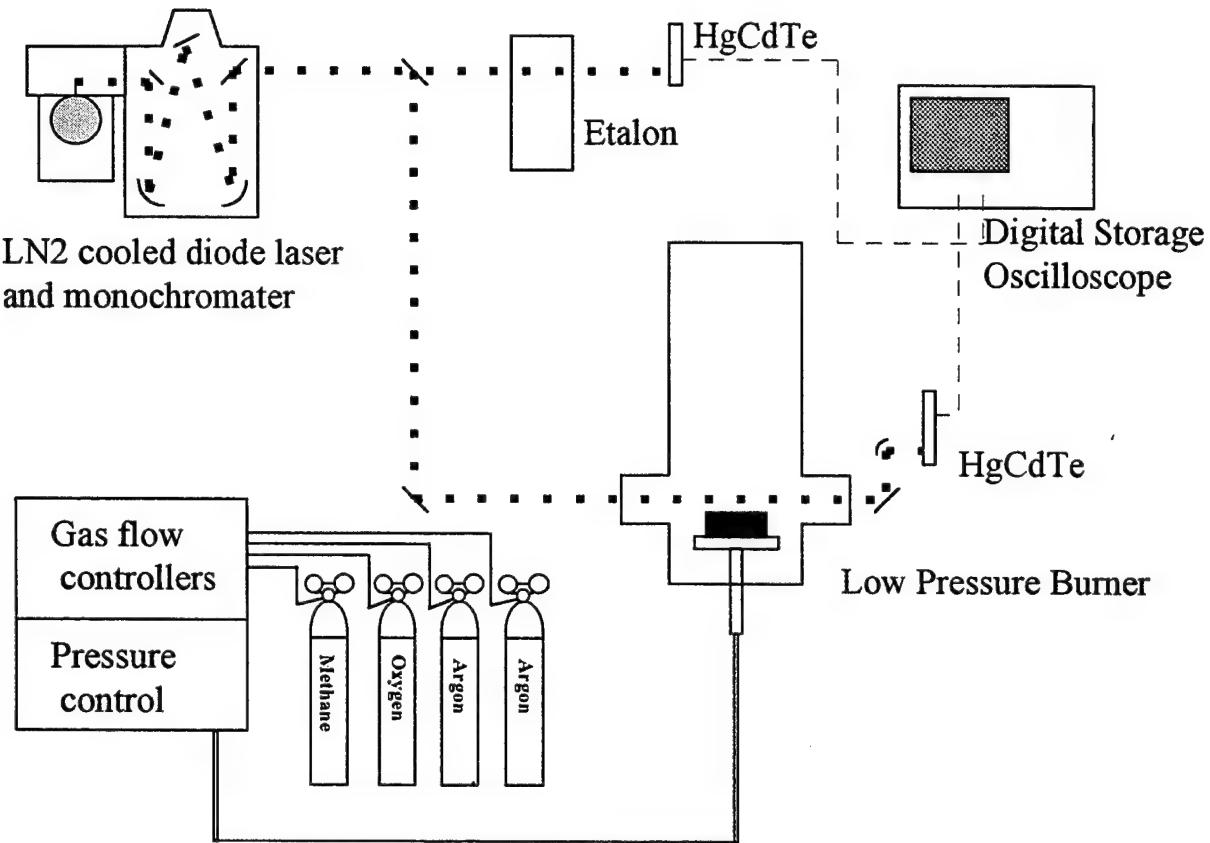


Figure 1. Schematic representation of the experimental apparatus.

a beam splitter, some beam steering and focusing optics, and the burner chamber, and impinges on an LN2-cooled HgCdTe detector. The split portion of the IR radiation passes through a passive confocal etalon that produces fringes as the frequency is scanned. The fringes allow the output of the diode to be monitored for nonlinearities and nonuniformities as the frequency is scanned. Data acquisition electronics receive signals from the IR detector.

The gas handling system consists of flow controllers for each of the gases introduced to the low-pressure burner chamber. A mass flow controller (MKS model 147B) is used to control flow meters (MKS model 2159B) that introduce the fuel (CH_4), oxidizer (O_2 or air), diluent (Ar), shroud gas (Ar), and inhibitor. The stated accuracy is $\pm 1\%$ of the full scale of the flow valve, so the maximum deviation is 0.1 L/min. The reproducibility is quoted as $\pm 0.2\%$ of the reading. We have found the flame characteristics to be very reproducible between experiments with this experimental setup. The inhibitor gas is mixed with the fuel flow at a Swagelok tee. The fuel/inhibitor mix is further mixed with the oxidizer and diluent at a Swagelok cross before entering a final mixing chamber in the burner head.

The low-pressure burner assembly consists of a flat flame burner (McKenna Industries, Inc.) mounted in a cylindrical vacuum chamber (Huntington Vacuum). The flat flame burner (Figure 2) is composed of concentric, sintered stainless steel fits through which the combustion and shroud gases flow. The flame front is supported above the fit. Its height above the fit is determined by the flame velocity, the pressure of the system, and the total flow rate of the gases. The shroud gas flow helps to stabilize the flame and to maintain laminar flow of the premixed gases. A thermocouple cemented to the burner head monitors its temperature. The head is mounted on both horizontal and vertical translation stages that provide for a full range of motion for spatial profiling of flame.

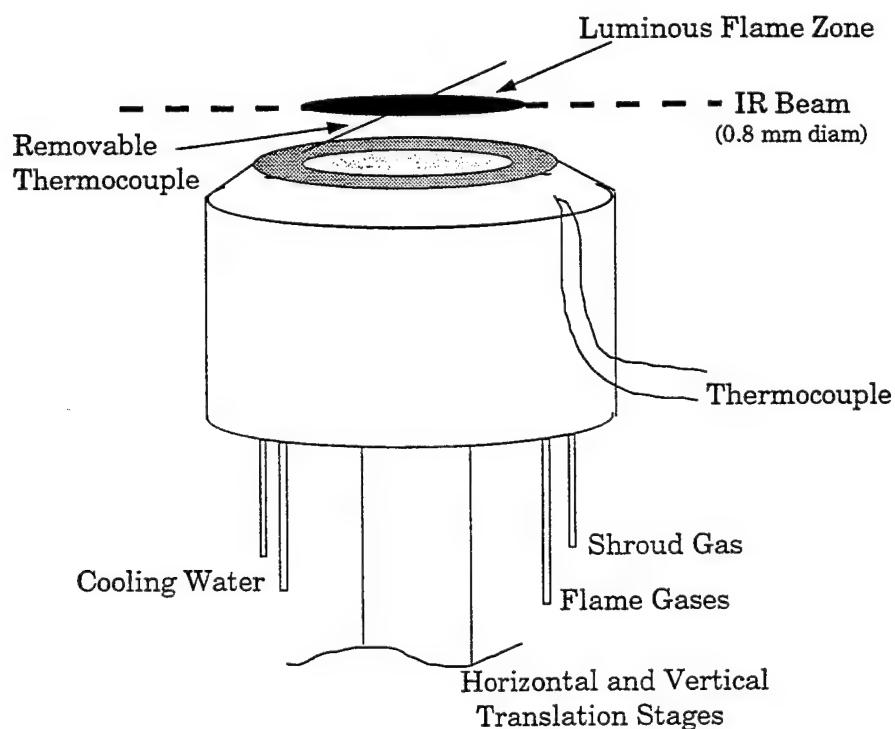


Figure 2. View of the flat flame burner assembly.

The exhaust gases are removed through the top of the low-pressure chamber by a Leybold SV-100 high-volume vacuum pump. They are removed from the top to further assist in maintaining laminar flow of the combustion gases. Coarse control over the chamber pressure is accomplished by a manual butterfly valve. Fine control of the pressure is obtained by a precision needle valve, open to the atmosphere, that is located just upstream to the butterfly valve. This combination of valves allows the pressure to be set and maintained to within several millitorr throughout the course of an experiment. The pressure of the chamber is measured at the base, below the burner head, by a 100-torr range capacitance manometer.

The data acquisition is accomplished using a LeCroy 9360 digital storage oscilloscope. The output of the IR detectors is passed through a preamplifier and then fed into the oscilloscope. The oscilloscope co-adds 500 scans, and then stores the spectrum on a diskette. Since the data are collected as single beam spectra, a background spectrum, consisting of a spectrum with no gases flowing, for each experiment is also collected. The data are transferred to a personal computer, converted to ASCII format, and analyzed to extract the temperature and/or concentration of the species under study.

Flame temperatures are also measured using Pt/10%Pt-Rh fine-wire (5 μm) thermocouples. As the flame temperature exceeds the melting point of platinum, the thermocouples are coated with a refractory mixture of yttrium oxide and beryllium oxide (Kent 1974). The high emissivity of this ceramic sheath reduces the internal temperature of the thermocouple junction. The sheath also minimizes errors caused by platinum-catalyzed reactions at the thermocouple junction.

3. DATA ANALYSIS

The identity of the absorbing species determines the method of analysis of the collected spectra. Carbon monoxide (CO) spectra are analyzed to obtain concentration profiles and to spectroscopically measure the temperature of the flame. The spectra are fit to a mathematical expression of the transmission, and both the concentration and temperature are extracted. The spectra of other flame species are analyzed for concentration information only, relying on the temperature from either the thermocouple or that measured by the CO spectra from that flame. The spectra of each molecule, from the available literature, are used to extract the concentration profiles, either relative concentration between different flames or absolute concentration whenever possible. Both methods are outlined in the subsequent sections.

3.1 Carbon Monoxide. The method known as two-line thermometry (Varghese and Hanson 1980) is used to determine the temperature and CO concentration profile of the flame under study. In this method, the temperature and the concentration of CO are extracted from the observation of two closely lying ro-vibrational transitions of CO originating from excited vibrational states. The flame temperature and CO concentration can be extracted from the ratio of the integrated absorbance of the two transitions.

The experimental transmission spectrum can be mathematically described by the Bouger-Lambert Law of Absorption (Varghese and Hanson 1980) as:

$$\tau(v) = \left(\frac{I}{I^0} \right) = \exp \left(- \left[S_{vJ}(T) \phi(v - v_0) L P_x \right] \right) \quad (1)$$

where $S_{vJ}(T)$ is the line strength of the transition, $\phi(v - v_0)$ is the line shape function, L is the path length of the absorbing species (nominally set by the dimension of the burner head), and P_x is the partial pressure of absorbing species x . The line strengths ($S_{vJ}(T)$) of the individual CO ro-vibration transitions have been calculated from a relation referenced to the literature value of the fundamental band strength of the transition (Varghese and Hanson 1980). The normalized single beam spectrum is fit to the following:

$$\tau(v) = \sum_i \exp \left(- \left[\alpha_i(T) V_i(a, \chi) \right] \right) + \Delta \quad (2)$$

where $\alpha_i(T)$ is the product of the line strength of the i^{th} transition with the pressure of the absorbing species, $V_i(a, \chi)$ is the Voigt function with the Voigt parameter and $\chi = (v - v_0)/v_D$, and Δ is a cubic baseline correction to account for the nonlinear output of the diode laser. The summation refers to the individual transitions present in the frequency range of the spectrum. A sample spectrum of CO is shown in Figure 3. The summation in equation 2 for this spectrum would thus include the CO P18(2,1) and the CO P12(3,2) transitions.

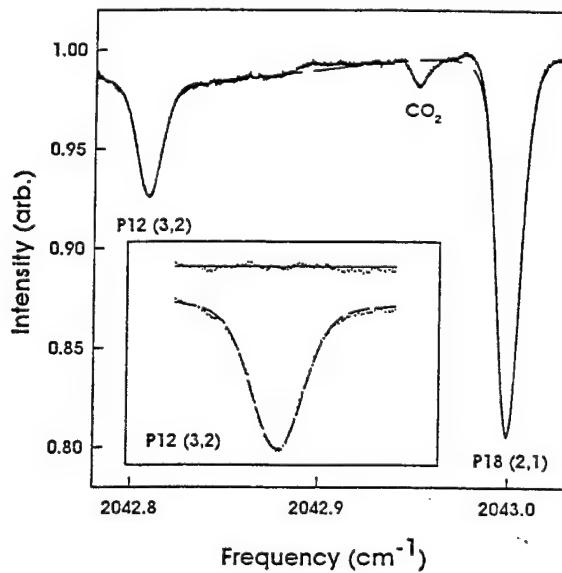


Figure 3. Sample spectrum of CO in a 20-torr flame. The inset shows a blowup view of the data plus fit, and the residual of the fit, of the P12 (3, 2) transition.

The observed CO spectrum is fit to the above equations using a nonlinear least-squares fitting routine (Bevington 1969). The Voigt profile is calculated using a summation approximation to the complex error probability function (Humliček 1979). T , α_i , a broadening parameter, a frequency shift for each transition, and the baseline parameters are the variables in this program. The temperature of the species being measured is determined from the ratio of the observed α_i by comparing this to values of the ratio of the calculated line strengths:

$$F(T) = \frac{S_{vJ}^{II}(T)}{S_{vJ}^I(T)} = \frac{\alpha^{II}(T)}{\alpha^I(T)}. \quad (3)$$

The pressure of the absorbing species is obtained from the definition of the α_i once the temperature has been calculated:

$$P_x = \frac{\alpha^I(T)}{S_{vJ}^I(T)}. \quad (4)$$

The calculated line strength values are used to construct the $F(T)$ found in equation 3. The goodness of the fit is measured by the chi squared test. Data sets for each flame and position within the flame are collected four times, and the results of the four sets are examined statistically for inconsistencies before being averaged to produce the final average value of temperature and concentration used as characteristic of the flame.

In a previous study, the final values of spectroscopically measured flame temperatures were consistently lower than the values measured by fine-wire thermocouples. In this study, the distribution of CO across the burner head was measured using tomographic analysis (McNesby, Daniel, and Mizolek 1995a). The flame temperatures obtained from the spectroscopic measurements are corrected to account for absorption by CO lying outside the burner region. The reduced absorbance of the individual transitions translates to a higher temperature than originally calculated. This is illustrated in Figure 4, in which thermocouple and spectroscopic temperatures (both corrected and uncorrected) are included. Figure 5 presents the CO concentration and temperature profiles of methane/oxygen flames inhibited with 1.0% of the fluoromethanes analyzed using two-line thermometry. It is readily seen from the figure that each agent produces unique behavior in the flame.

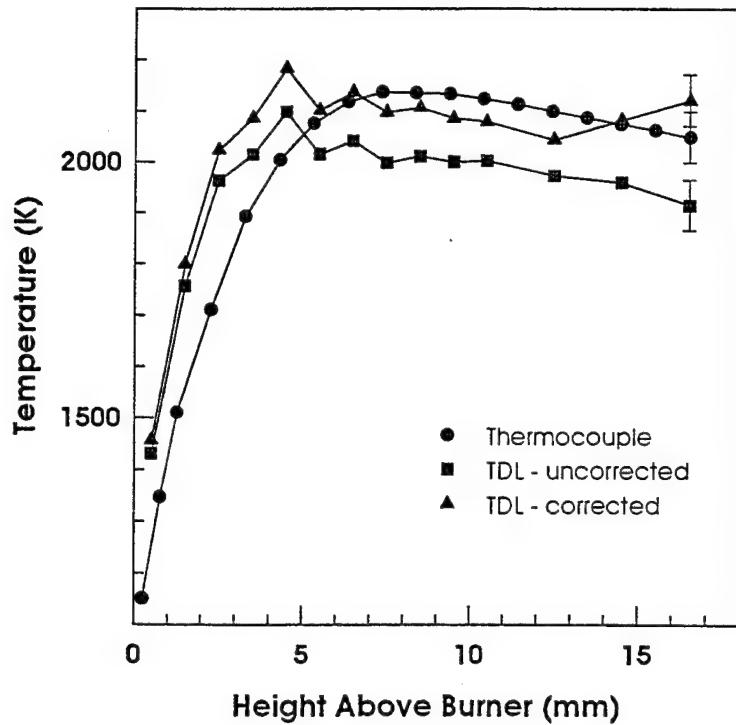


Figure 4. Flame temperature profiles of an inhibited methane/oxygen flame measure spectroscopically and with fine wire thermocouples.

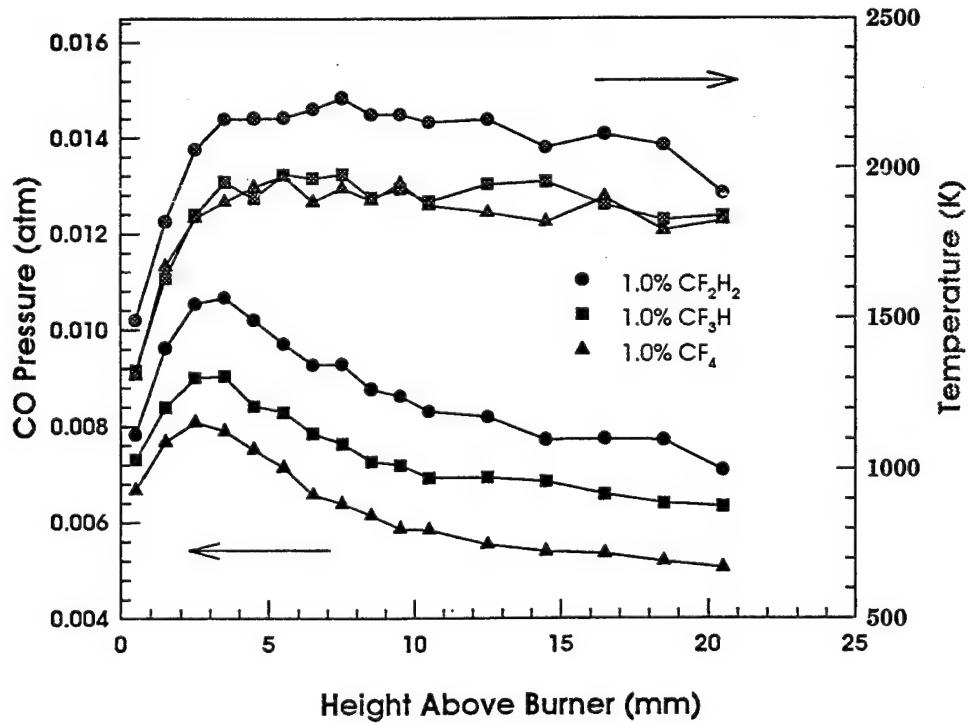


Figure 5. CO concentration and temperature profiles of 20-torr, stoichiometric, premixed methane/oxygen flames inhibited with 1.0% of the fluoromethanes.

3.2 Other Species. The concentration profiles of the other species, observed using IR absorption spectroscopy and employing the LeCroy 9360 digital oscilloscope, are analyzed by either of two methods. The first method obtains relative concentrations of the species by integrating the normalized absorbance of a specific transition of the molecule being studied. The spectrum of one or more individual ro-vibration transitions is collected for flames doped with each of the inhibiting compounds being studied. The spectrum is then normalized by taking a ratio with respect to a background spectrum collected with no gas flow. This normalization procedure accounts for differences in the diode laser output power, which varies day to day. The area of the normalized spectrum is then determined by numerical integration before being compared with the values from the other flames.

These relative intensities can be compared for flames containing different inhibitor and different inhibitor amounts. Figures 6 and 7 show the relative disappearance profiles of CH_4 and appearance profiles of H_2O for both an uninhibited flame and flames doped with 1% of the inhibitors Halon 1301 (CF_3Br), HFC-125 ($\text{C}_2\text{F}_5\text{H}$), and FE-13 (CF_3H). The pressure of these flames was 32 torr. As seen in Figures 6 and 7, the effects of the inhibiting agent on the relative population of the observed species are unique to each agent. For example, in Figure 6, the lowest trace is the disappearance profile of CH_4 in an uninhibited flame. In the other three flames, the amount of methane is higher at each position above the burner, indicating that the methane is reacting at a slower rate than in the uninhibited flame. Thus, the rate of disappearance of CH_4 is slower in each of the doped flames, as evidenced by the higher relative population of CH_4 in the inhibited flames. However, the rate of appearance of H_2O does not decrease for all the agents. Halon 1301 actually increases the rate of appearance. It is this type of information, the differences in the chemistry of the flame, which is used in making qualitative comparisons with the modeling results. Figure 8 is another illustration of the changes in the characteristics of the flames. In a 20-torr flame, the flame front's position, stabilized above the burner as a function of the flame speed, visibly shifts, indicating a reduction of the flame speed. The change in the flame front position is another example of a qualitative effect that can be compared to modeling results.

The second method, presently under development, determines the absolute concentration of the species of interest by using the line strength of the transition examined. This approach requires both the identification of the transition and the species temperature. The transition is identified by comparison with exact line positions from the literature, and the temperature of the species is determined either from the fine-wire thermocouples or spectroscopically, where the flame temperature is assumed to equal the species temperature. By fitting a mathematical model of the lineshape of the transition, an absolute concentration

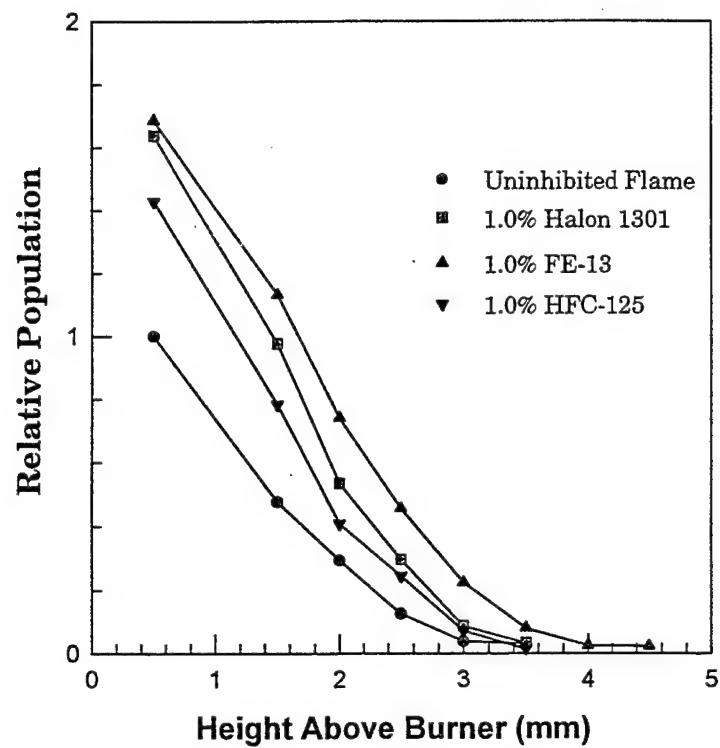


Figure 6. Disappearance profiles of methane in a 32-torr inhibited flames relative to an inhibited flame.

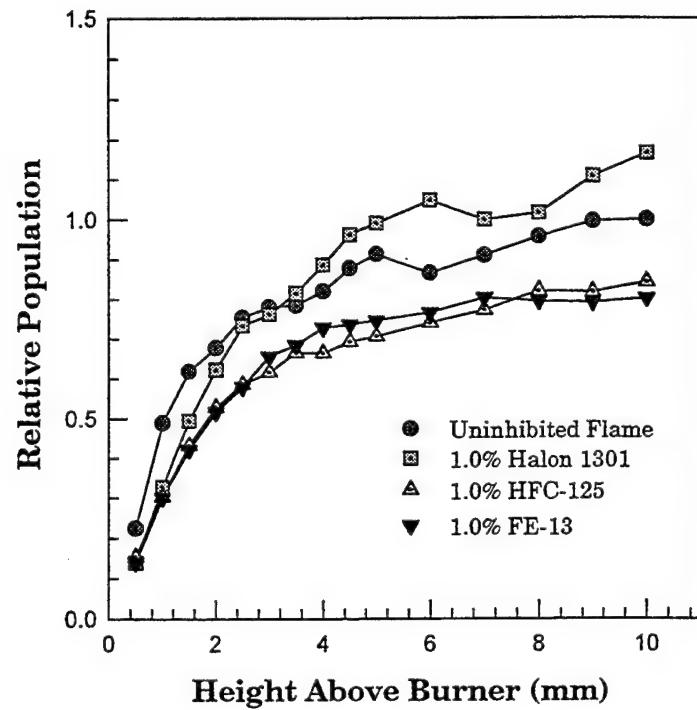


Figure 7. Appearance profiles of water in 32-torr inhibited flames relative to an inhibited flame.

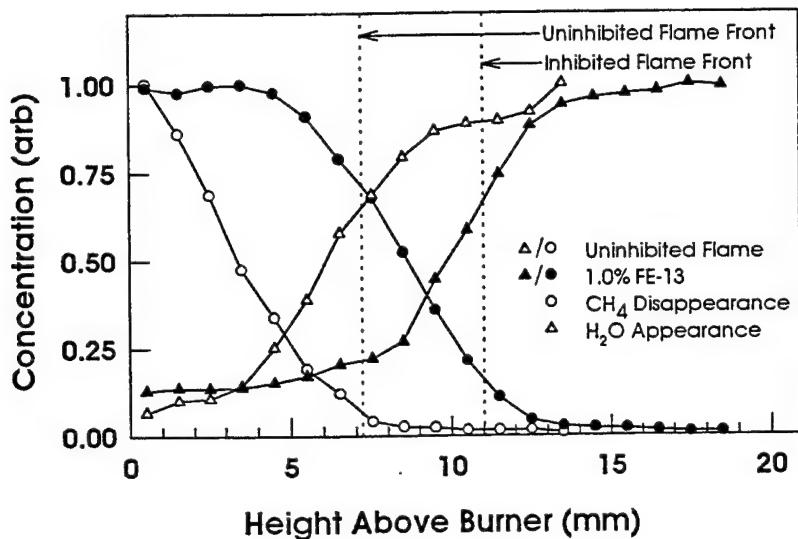


Figure 8. Methane disappearance profiles (circles) and water appearance profiles (triangles) for an inhibited flame and a flame inhibited with 1.0% CF_3H . The shift in the flame front away from the burner is attributed to a decrease in the flame speed.

of the species can then be extracted. The molecules presently being studied for absolute concentration using this method are CH_4 , H_2O , and CF_2O .

Even without absolute concentrations for all species observed, the information obtained has proven useful for the validation of the chemical kinetic mechanism describing fluorine chemistry in flames (Linteris and Gmurczyk 1995; Babushok et al. 1995). Figure 9a shows the calculated disappearance profiles of three fluoromethane agents in a 20-torr, freely propagating methane/air flame. Figure 9b shows the observed relative disappearance profiles of the same agents in a 20-torr burner stabilized methane/oxygen flame. Qualitative agreement is easily seen, though the calculations are not yet directly comparable. Work continues on the modeling to incorporate the experimental conditions to allow for direct comparison with the experimental results.

Figure 10 presents the appearance profiles of CF_2O in flames inhibited with two candidate halon replacement compounds, FE-13 (CF_3H) and HFC-125 ($\text{C}_2\text{F}_5\text{H}$), and with Halon 1301 (CF_3Br) for comparison. The profiles show that more CF_2O , a toxic byproduct of the combustion process of fluorine-containing flames, is produced by both alternate agents than by Halon 1301. Other qualitative differences in the activity of these agents are illustrated in Figures 11a-d, which show an uninhibited flame and flames inhibited with 1.0% of the three agents near $1,259.2\text{ cm}^{-1}$. The most obvious change is the

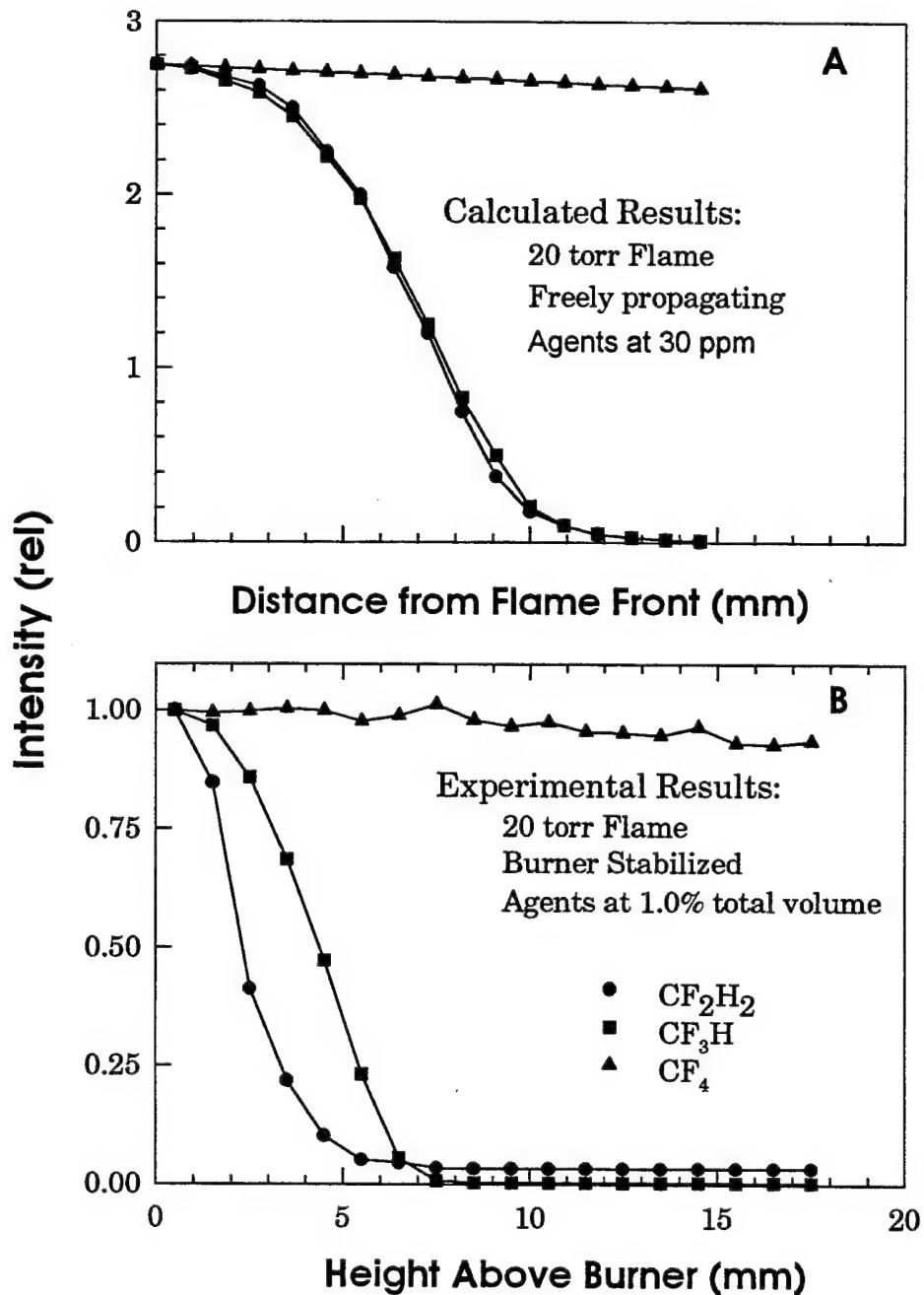


Figure 9. A) Calculated disappearance profiles of the fluoromethanes in a freely propagating, 20-torr methane/oxygen flame. The flame front is at 0 mm. B) Experimental disappearance profiles at the fluoromethanes in burner stabilized, 20-torr methane/ oxygen flames. The flame front is at 4 mm for all three flames.

intensity of the two water transitions. (Each of the spectra in Figure 11 is a scan of 0.25 cm^{-1} ; yet, in the narrow region, transitions of three different molecules are readily observed and easily separated.) The intensity of the methane transition also increases upon the addition of all three agents. This change occurs because the agents cause a change in the species temperature within the flame, thus changing the population distribution among the molecular energy levels. Also shown are the differing amounts of CF_2O produced. Figure 11 also clearly illustrates the strength of the TDLAS technique in observing individual molecules in spectrally congested regions.

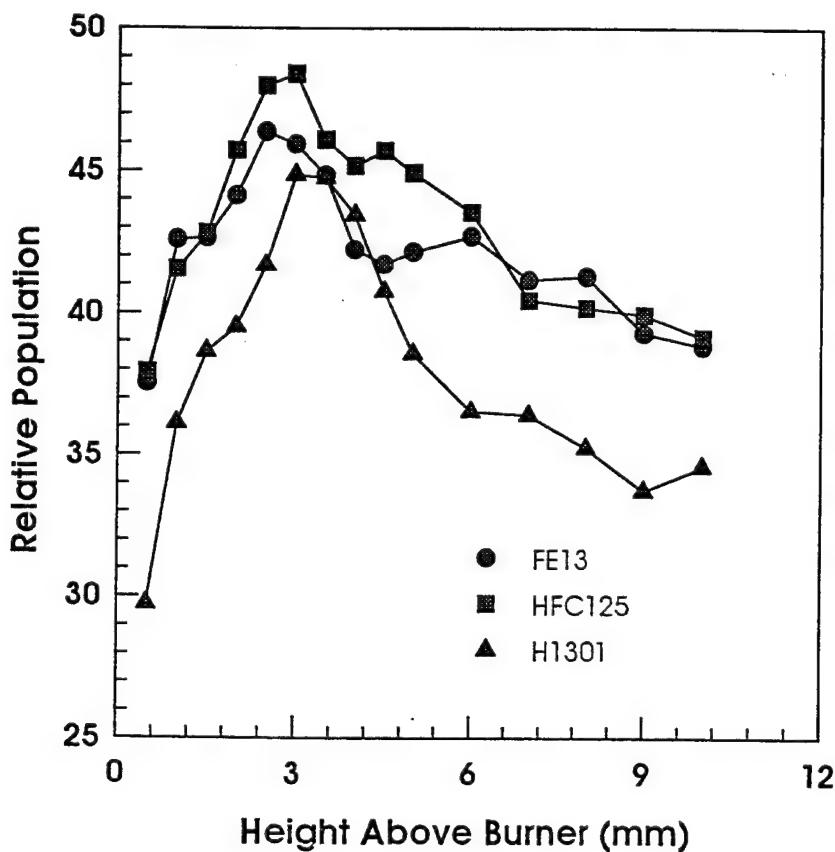
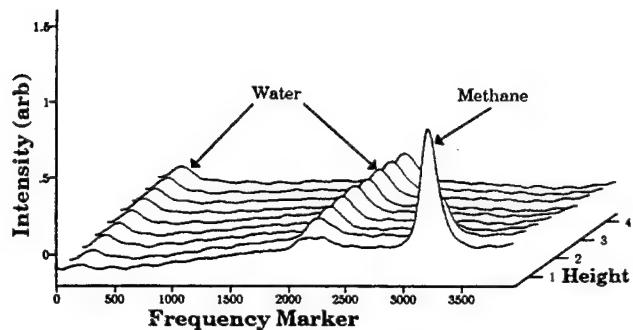
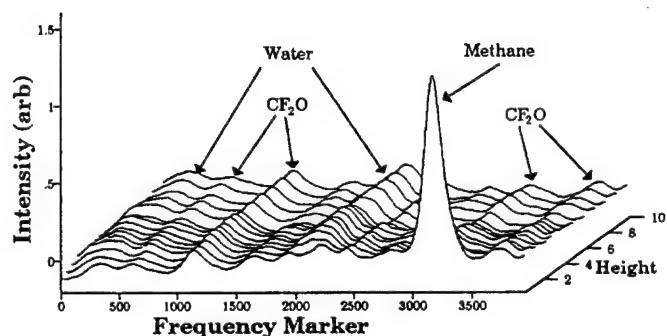


Figure 10. Appearance profiles of CF_2O for 32-torr methane/oxygen/argon flames inhibited with agents at 1.0% total volume.

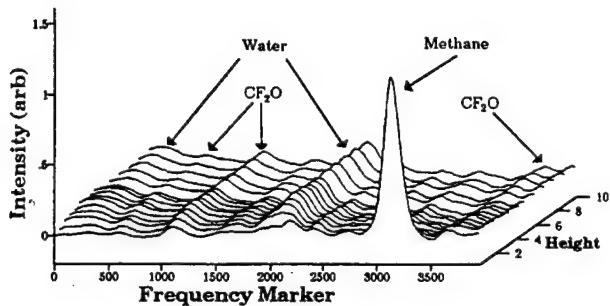
A)



B)



C)



D)

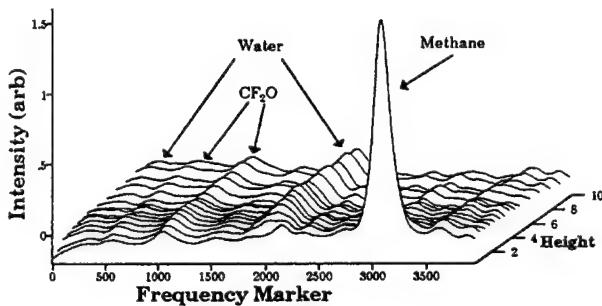


Figure 11. Three-dimensional spectral profile of methane/oxygen/argon flames at $1,259.2\text{ cm}^{-1}$ as a function of height above the burner in millimeters. A) Inhibited flame. B) Flame inhibited with 1.0% HFC-125. C) Flame inhibited with 1.0% FE-13. D) Flame inhibited with 1.0% Halon 1301.

4. CONCLUSIONS

We have obtained both qualitative and quantitative concentration profiles of combustion species in low-pressure, premixed flames inhibited with halon-alternate compounds and with Halon 1301. Flame temperature profiles have also been measured both with fine-wire thermocouples and spectroscopically using the method of two-line thermometry. The data are presently being used in the validation of a

chemical kinetic mechanism that describes halogenated flames. This study has also shown the versatility of TDLAS in the characterization of combustion systems where a line-of-sight technique can be applied, and with the availability of IR transmitting fibers, virtually any combustion system can be analyzed using tunable diode lasers. We have observed 11 flame species present in the combustion system, and are continuing to expand this number.

Through this project, we are expanding the understanding of the fundamental processes that govern flame inhibition. This work continues along the following paths: the inclusion of other combustion species, including important radical species ($\text{CF}_2\cdot$ and $\text{CF}_3\cdot$) (McNesby, Daniel, and Mizolek 1995b) the application of TDLAS to diffusion flames (McNesby et al. 1996) coupling with modeling (Smooke 1994, 1995) of these flames, and the inclusion of a room temperature near-IR laser system for the detection of the acid gas HF in combustion systems. The use of near-IR lasers for acid gas detection has shown promise as another technique for monitoring combustion processes and the byproducts of halogenated flames (Bomse et al. 1992).

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